

DECLARATION

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do hereby solemnly and sincerely declare:

- 1) THAT I am well acquainted with the Japanese language  
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- 2) THAT the attached is a full, true, accurate and  
faithful translation into the English language made  
by me of Japanese Patent Application No. 2002-236862.

The undersigned declares further that all  
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believed to be true; and further that these statements  
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Signed this 12<sup>th</sup> day of September, 2008



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[Kind of Document] Description

[Title of the Invention] ELECTRODE CATALYST

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[Claim 1]

5                   An electrode catalyst characterized by  
comprising a catalyst supported on a conductive carrier,  
wherein said catalyst is a mixture of a particulate  
silver and at least one particulate rare-earth oxide.

[Claim 2]

10                   The electrode catalyst according to claim 1,  
characterized in that the conductive carrier is a  
particulate carbon.

[Claim 3]

15                   The electrode catalyst according to claim 1,  
characterized in that the rare-earth oxide is cerium  
oxide, holmium oxide or gadolinium oxide.

[Claim 4]

20                   The electrode catalyst according to claim 3,  
wherein the molar ratio of the silver to the rare-earth  
oxide is from 1 : 0.5 to 1 : 2.0.

[Claim 5]

                  A gas diffusion electrode for brine  
electrolysis, characterized by use of the electrode  
catalyst according to any of claims 1 to 4.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an electrode  
5 catalyst, particularly an electrode catalyst suitable  
for a gas diffusion electrode, and a process for  
preparing the electrode catalyst. More specifically,  
the invention relates to an electrode catalyst suitable  
for a gas diffusion electrode for oxygen reduction,  
10 applicable to an oxygen cathode for brine electrolysis,  
a metal-air battery, or the like.

[0002]

[Prior Art]

A gas diffusion electrode allows a gas such as  
15 hydrogen, oxygen, or air to be supplied to a porous  
electrode and to react on the electrode. The gas  
electrode is used in a fuel cell, a metal-air battery or  
the like which converts the chemical energy of gas to  
electric energy.

20 In the field of brine electrolysis, a gas  
diffusion electrode in the form of a cathode that is  
capable of realizing energy-saving is being developed.  
This development is under way because a cathodic  
reaction that can change from a current hydrogen  
25 generation reaction to an oxygen reduction reaction will  
produce a significantly reduced electrolysis voltage.

[0003]

Various gas diffusion electrodes are known for

specific applications. The gas diffusion electrode, which is known to use an electrolyte solution in the form of an aqueous solution, is a laminated structure between gas diffusion and reaction layers, in the inner  
5 part of which a collector for electrical connection is embedded. Oxygen is supplied from the side of the gas diffusion layer, and the reaction layer is in contact with the electrolyte. After permeating the gas diffusion layer for diffusion in the inside, oxygen is  
10 subjected to a reduction reaction on an oxygen reduction catalyst fixed in the reaction layer.

Previously known catalysts which are high oxygen reduction activity include platinum, silver, organometallic complexes, perovskite oxides, or the like  
15 (JP-A-2000-212788; F. C. Anson, et al., J. Am. Chem. Soc., 1980, 102, 6027; JP-A-02-257577; and JP-A-07-289903). These catalysts mainly use a carbon particle as a carrier, and are supported on it in a highly dispersed condition.

20 [0004]

The gas diffusion electrode for brine electrolysis has a limited kind of electrode catalysts, since they are employed in an atmosphere of an aqueous caustic soda solution with a concentration of 30% by  
25 weight or more, which means a severe environment giving corrosion to even a noble metal such as platinum. Silver is only a substance, which has been confirmed in stability of long-term continuous operation (N. Furuya

and H. Aikawa, Electrochim. Acta, 45 4251 (2000)).

However, the catalytic activity of silver is not sufficient, and the use of silver as a cathode leads to elevated overvoltages. As a result, the oxygen cathode system cannot enjoy the documents of the current hydrogen cathode system, in view of the costs including the oxygen cost. Thus, there is a need for a catalyst with higher oxygen reduction activity in the art.

[0005]

10 [Problems to be Solved by the Invention]

An object of the present invention contemplates the provision of an electrode catalyst with higher oxygen reduction activity than a conventional catalyst of silver.

15 [0006]

[Means for Solving the Problem]

As the result of earnest and repeated research for solving the above described problems, the present inventors have found that an electrode catalyst, which contains a mixture of a particulate silver and at least one particulate rare-earth oxide, exhibits more enhanced oxygen reduction activity than an electrode catalyst containing only silver. Thereby, the present invention is accomplished.

25 Thus, the present invention is as follows:

(1) An electrode catalyst characterized by comprising a catalyst supported on a conductive carrier, wherein the catalyst is a mixture of a particulate



silver and at least one particulate rare-earth oxide.

(2) The electrode catalyst described in item (1), characterized in that the conductive carrier is a particulate carbon.

5 (3) The electrode catalyst described in item (1), characterized in that the rare-earth oxide is cerium oxide, holmium oxide or gadolinium oxide.

(4) The electrode catalyst described in item (3), wherein the molar ratio of the silver to the rare-  
10 earth oxide is 1:0.5 to 1:2.0.

(5) A gas diffusion electrode for brine electrolysis, characterized by use of the electrode catalyst described in any of the items (1) to (4).

[0007]

15 The present invention is described below in detail.

The electrode catalyst of the present invention is an electrode catalyst including a catalyst supported on a conductive carrier, wherein the catalyst  
20 is a mixture of a particulate silver and at least one particulate rare-earth oxide. The invention provides an electrode catalyst, which supports a mixture of a particulate silver and at least one particulate rare-earth oxide, with higher oxygen reduction activity than  
25 only a particulate silver. Specifically, according to the electrode catalyst of the invention, the interface between the particulate silver and the particulate rare-earth oxide provides a reaction active site and produces

enhanced oxygen reduction activity due to promoter effect by the rare-earth oxide.

[0008]

According to the invention, as long as it is  
5 fixed to the carrier, a smaller silver particle, which  
is the main catalyst, is preferred because the surface  
area of the silver which is the main catalyst, is  
increased. Particularly, the particle diameter is  
preferably 200 nm or less, more preferably 100 nm or  
10 less. If the particle diameter is too large, i.e. more  
than 200 nm, the surface area of the silver, which is  
the main catalyst, is decreased, the satisfactory oxygen  
reduction activity is unable to be achieved. Also, when  
the size of the rare-earth oxide fixed to the carrier  
15 decreases, the number of the active sites is increased,  
which is preferable. Particularly, the particle  
diameter is preferably 500 nm or less. If the particle  
diameter is too large, i.e. more than 500 nm, the  
interface serving as the active site is less easily  
20 formed, and the satisfactory oxygen reduction activity  
is not achieved.

[0009]

The electrode catalyst of the present  
invention is typically supported on a conductive carrier  
25 with large surface area for the purpose of the  
enlargement of the surface area of the catalyst.

Typically, as the conductive carrier, a fine  
particulate carbon is used. For example, a carbon black

with a BET specific surface area of 30 to 2,000 m<sup>2</sup>/g may be cited. The so-called furnace black, lamp black, acetylene black, channel black, thermal black, or the like may be used. Preferably, the carbon particle has a diameter of 0.01 μm to 1 μm.

[0010]

Rare-earth oxides used for the invention include the oxide of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or the like, and are preferably cerium oxide, holmium oxide, and gadolinium oxide.

When the amounts of presence of a particulate silver and at least one particulate rare-earth oxide are set to A and B, respectively, the compositional ratio between the particulate silver and the at least one particulate rare-earth oxide contained in the electrode catalyst of the invention is preferably 0.5 to 2.0 in a molar ratio of B to A (B/A). A molar ratio of less than 0.5 will result in an insufficient amount of the particulate rare-earth oxide, and thus will lead to poor formation of the interface providing the active site. Conversely, a molar ratio of more than 2.0 will result in an excessive amount of rare-earth oxide, producing a structure in which the rare-earth oxide covers up the particulate silver, and again will lead to a reduced interface. In both instances, oxygen reduction activity

cannot be enhanced.

[0011]

The proportion of the electrode catalyst substance is preferably 10 to 90% by weight, based on  
5 the weight of the particulate carbon. An insufficient amount of the electrode catalyst substance will result in the reduced total reaction surface area of the substance, and thus will not produce sufficient oxygen reduction activity. Alternatively, an excessive amount  
10 of the electrode catalyst substance will result in the substance becoming prone to flocculate, lead to reducing the total reaction surface area of the substance, and thus not producing sufficient oxygen reduction activity.

[0012]

15 The process for preparing the electrode catalyst of the invention is described below.

(1) A method for supporting silver

First, a method for supporting a particulate silver will be described. A particulate carbon powder  
20 is generally used as a conductive carrier. The case of employing the powder as the carrier is described below.

In a dispersion step, a particulate carbon powder is first dispersed in a solution in which silver salt is dissolved. The silver salt may be any silver  
25 salt capable of being dissolved in a solvent, including the nitrate, chloride, sulfate, carbonate, or acetate of silver. The silver nitrate is preferable since chlorine, sulfur or the like is hard to be a residue at

thermal decomposition.

[0013]

The solvent used is generally water.

Optionally, a small amount of alcohol, organic solvent,  
5 acid, alkali, or the like may be also employed. Any  
solvent in which silver salt can be dissolved may be  
used.

In order to disperse the particulate carbon  
powder in the solution, various methods may be used,  
10 including agitation using a stirrer or a stirring rod,  
use of a kneader, ultrasonic dispersion, use of a  
homogenizer, use of an ultrasonic homogenizer, or the  
like. The method involving agitation using a stirrer is  
typically employed because of its ease at use.

15 In a drying step, the suspension is then  
evaporated to dry. The drying method may be any method  
by which the solvent can be removed, including retention  
in a dryer or an oven at around 100°C for 12 hours or  
more, use of a vacuum dryer, an evaporator, or the like.

20 [0014]

In a firing step, a catalyst precursor, which  
is the dispersion of the silver nitrate and the  
particulate carbon obtained in the drying step, is  
subjected to thermal decomposition reaction to provide a  
25 silver-loaded carbon powder having the highly dispersed  
particulate silver. In order to avoid progression of  
oxidation of the particulate carbon of the conductive  
carrier, heating is preferably carried out in a non-

oxidative atmosphere of nitrogen or the like. However, if the particulate silver can be formed at such a low temperature that the carbon particle is not oxidized, heating can be performed even in air or an atmosphere  
5 containing oxygen. The temperature used during firing, at which the silver is formed by thermal decomposition, is preferably as low as possible. The preferred firing temperature is 200 to 700°C. If firing is performed at too high temperature, then the particulate silver will  
10 flocculate, resulting in a larger diameter of the silver. Alternatively, if firing is carried out at too low temperature, then the thermal decomposition of silver salt will not completely occur, thus, producing no particulate silver. Firing/thermal decomposition  
15 time is preferably 1 to 10 hours.

After the heat treatment, the silver-loaded carbon powder is optionally pulverized. Thereafter, the silver-loaded carbon powder pulverized may be used for preparing a gas diffusion electrode, or further for  
20 supporting a metal oxide. The pulverization may be carried out by various methods using a mortar, various mills, or the like.

[0015]

(2) A method for supporting rare-earth oxide

25 A method for supporting a particulate rare-earth oxide is then described.

In a dispersion step, a carbon powder is first dispersed in a solution containing rare-earth salt. The

rare-earth salt is preferably a nitrate because the nitrate is subjected to firing in an atmosphere of an inert gas in a firing step to provide rare-earth oxide.

In order to disperse the silver-loaded carbon powder in this solution, various methods may be used, including agitation using a stirrer or a stirring rod, use of a kneader, ultrasonic dispersion, use of a homogenizer, use of an ultrasonic homogenizer, or the like. The method involving agitation using a stirrer is typically employed because of its ease of use.

[0016]

This solution may be dried in a subsequent drying step. However, an alkali such as sodium hydroxide or ammonia may also be added to form a hydroxide, followed by evaporation to dryness.

In a drying step, the suspension is then dried. The drying method may be any method by which the solvent can be removed, including retention in a dryer or an oven at around 100°C for 12 hours or more, use of a vacuum dryer, an evaporator, or the like.

[0017]

In a firing step, the electrode substance obtained from the drying step is subjected to thermal decomposition reaction to support, on the carbon, the rare-earth oxide. In order to avoid progression of oxidation of the particulate carbon of the conductive carrier, heating firing is preferably carried out in a non-oxidative atmosphere of nitrogen or the like.

However, if a particulate rare-earth oxide can be formed at such a low temperature that the carbon particle is not oxidized, heating can be performed even in air or an atmosphere containing oxygen. The firing temperature, at which the rare-earth oxide is formed by thermal decomposition, is preferably as low as possible. The preferred firing temperature is 200 to 1,000°C. In addition, retention time is preferably 1 to 10 hours. If firing is performed at too high of a temperature, then the particulate rare-earth oxide will flocculate, resulting in a larger diameter thereof. Alternatively, firing at too low of a temperature is unfavorable because the thermal decomposition of rare-earth nitrate will not completely occur to produce the residue thereof.

[0018]

After the heat treatment, the powder prepared is optionally pulverized. Thereafter, the powder pulverized may be used for preparing a gas diffusion electrode, or further for supporting a metal or a metal oxide. The pulverization may be carried out by various methods using a mortar, various mills, or the like.

In order to prepare the electrode catalyst of the invention, (1) a particulate silver is supported on a particulate carbon powder, and (2) a particulate rare-earth oxide is supported on the powder. However, step (1) and step (2) may be performed in any order: the particulate silver may be formed on the particulate



carbon, followed by supporting the particulate rare-earth oxide, or the particulate rare-earth oxide may be formed on the particulate carbon, followed by supporting the particulate silver. Further, the particulate silver and the particulate rare-earth oxide may be supported simultaneously, using a mixed solution of silver salt and rare-earth salt. In addition, many kinds of rare-earth oxides and silver may be supported.

[0019]

10 In addition to the above methods, the supporting on the conductive carrier may be carried out using a colloidal solution of silver or rare-earth oxide, or a suspension having powder dispersed in a solvent.

15 Of the electrode catalyst obtained through these steps, the crystal structure may be determined using powder X-ray diffractometry. The diameter thereof can be found through the observation with the electron microscope.

20 The electrode catalyst obtained by these methods was evaluated using a channel flow electrode method (referred as CFDE later). The measuring cell shown in Fig. 1 was employed for the measurement based on CFDE. The measuring cell indicated in Fig. 1 has a structure in which an oxygen-saturated electrolyte is introduced at an electrolyte inlet 5, passed through an electrolyte passage 6 with a thickness of 0.05 mm, and discharged at an electrolyte outlet 7. Under this

situation, the flow of an electrolyte contacting a working electrode 1 and a detecting electrode 2 is adequate if being in the form of a laminar flow. The acrylic resin plate has a cavity  $2 \times 5$  mm in area, 2 mm in depth in a part thereof, and the cavity, filled with an electrode catalyst, is rendered the working electrode 1. The detecting electrode 2 made of platinum  $1 \times 5$  mm in area with smooth surface is located by the gap of 0.25 mm from the working electrode 1. The working electrode 1 and the detecting electrode 2 have a working electrode wiring 3 and a detecting electrode wiring 4, respectively, for electric connection. A liquid-junction portion 8 with a reference electrode is also provided. The diffusion rate of dissolved oxygen in the electrolyte can be controlled by changing the flow rate of the electrolyte. The electrolyte is flowed at a fixed flow rate to allow oxygen reduction reaction to occur on the working electrode 1. The detecting electrode 2, which is set at such an electric potential that  $\text{HO}_2^-$  can be oxidized, oxidizes  $\text{HO}_2^-$ , which is an intermediate produced by the working electrode 1, to detect the resultant as an oxidation current. The electrolyte is flowed at a constant rate to allow a potential-current curve of the working electrode 1 to be measured. In the measurement, if the higher the electric potential is, the more the oxygen reduction current flow, it can be concluded that such an electrode catalyst has a higher oxygen reduction activity.

Further, the ratio of 2-electron reaction to 4-electron reaction can be obtained from current values of the working electrode and the detecting electrode.

[0020]

5               Further, a gas diffusion electrode was prepared and electrode characteristics were evaluated for studying the performance of the electrode catalyst as the gas diffusion electrode.

              The gas diffusion electrode is a laminated  
10   structure between a gas diffusion layer and a reaction layer, inside which a collector for electric connection is embedded. Oxygen is supplied from the gas diffusion layer side, and the reaction layer is in contact with an electrolyte. After permeating through the gas diffusion  
15   layer and diffusing therein, the oxygen is subjected to reduction reaction on the oxygen reduction catalyst fixed to the reaction layer.

[0021]

              In the gas diffusion layer, it is necessary  
20   that the oxygen gas can permeate rapidly through this layer and can diffuse uniformly in the whole reaction layer, and the diffusion layer is also required to serve to inhibit the penetration of the electrolyte from the reaction layer side. Anything in which these two  
25   functions are satisfied may be used. However, a powder may be employed here, obtained by mixing and dispersing a carbon particle in a suspension of a fluororesin such as polytetrafluoroethylene with high water repellency

before filtration and drying. Preferably, the carbon particle in the gas diffusion layer uses a carbon particle having a high water repellency and a large particle diameter.

5 [0022]

In the reaction layer, it is necessary that a catalyst for oxygen reduction be fixed while it is highly dispersed and the area of a three-phase interface among oxygen, the oxygen reduction catalyst, and the electrolyte be formed in a sufficiently large size. The powder for reaction layer may use a pulverized powder which is obtained by mixing the carbon particle supporting the electrode catalyst according to the process for preparation of the present invention with a suspension of a fluororesin such as polytetrafluoroethylene and dispersing the mixture using a dispersion solvent such as alcohol before filtration and drying.

The collector may be any material which has a sufficient electric conductivity for electrical connection, and does not produce dissolution, corrosion, or the like in an electric potential in which oxygen reduction reaction occurs. A metal gauze such as nickel or silver, a foam, or the like may be used.

25 [0023]

The gas diffusion electrode may be prepared by: providing a nickel gauze or the like for a collector in a die in prescribed form; packing powder particles

for gas diffusion layer on the collector followed by cold pressing; and then, packing powder particles for reaction layer followed by cold pressing; and finally melting polytetrafluoroethylene by hot pressing for  
5 integration.

The gas diffusion electrode obtained by the above method may be inserted into a cell for evaluating electrochemical characteristics, and allowed to effect an oxygen reduction reaction through supplying oxygen or  
10 air from the gas diffusion layer side to measure an electrode potential in each current density in order to evaluate the electrode performance.

[0024]

#### [Examples of the Invention]

15 The present invention is described in further details, based on Examples. However, the invention is not intended to be limited in any manner by these Examples.

[0025]

#### 20 [Example 1]

(Preparation of a silver-loaded carbon)

A carbon containing 50% by weight of silver was prepared as described below.

Two grams of carbon black (from Mitsubishi  
25 Chemical Corporation: Ketjen Black EC-600JD) ground by using a mill (from Janke & Kunkel Co.: A10) and 3.15 g of silver nitrate (from Wako Pure Chemical Industries Ltd.) were dispersed in 200 ml of an aqueous solution.

This dispersion was stirred for 15 minutes using a stirrer, and then subjected to the evaporation of the water content in an oven at 100°C, followed by drying to provide a powder. Subsequently, this powder was  
5 subjected to firing in a stream of nitrogen at 250°C for one hour, to thermally decompose silver nitrate, and then this powder was ground by using the mill to provide a carbon containing 50% by weight of silver.

[0026]

10                   0.434 g of cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , from Wako Pure Chemical Industries Ltd.) was then added to 0.216 g of the silver-loaded carbon powder to provide a silver to cerium molar ratio of 1 : 1, followed by dispersion in water to perform ultrasonic dispersion for  
15 5 minutes. Further, the water content was evaporated in an oven at 100°C, followed by drying to provide a sample powder. This powder was subjected to firing in a stream of nitrogen at 800°C for one hour, and ground by using the mill to provide an electrode catalyst powder. The  
20 powder X-ray diffraction of the electrode catalyst powder was performed. Specifically, using RINT-2500 (from Rigaku Corporation), the radiation source employed was copper  $\text{K}\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Identification of a peak provided the detection of Ag and  $\text{CeO}_2$ .

25 [0027]

The observation of the micro-structure was performed with the high resolution analysis transmission electron microscope (from JEOL Ltd.: JEM4000FX). As a

result, Ag with a size of 50 to 100 nm, and particles of  $\text{CeO}_2$  were found.

A small amount of liquid paraffin (from Kishida Chemical Co., Ltd.) was added to the electrode catalyst powder thus prepared, followed by mixing in a mortar to produce a paste. This paste was packed in a working electrode portion of CFDE. A platinum wire and a silver/silver chloride electrode were rendered a counter electrode and a reference electrode, respectively. Bubbling was carried out in a 0.1 M aqueous sodium hydroxide solution with pure oxygen for one hour to make this aqueous sodium hydroxide solution oxygen-saturated. In addition, the solution, the flow rate of which was fixed at 83.2 cm/sec, was kept at -0.6 V for 10 minutes, and the working electrode was then swept at 10 mV/sec from the potential +0.1 V to -0.6 V to measure a potential-current curve. The evaluation results obtained are depicted in Fig. 2. A higher oxygen reduction activity is shown.

[0028]

Further, when the potentials of the working electrode and the detecting electrode are fixed at -0.6 V and 0.5 V, respectively, and the flow rate is changed to 41.6, 83.2, 124.8 and 166.4, the corresponding current values of the working electrode and the detecting electrode were measured. The number of the reaction electrons were calculated from the ratio of the currents of the working electrode to the detecting

electrode with the following formula. The number of the reaction electrons represent how many electrons flow for one oxygen. The closer to 4 the value is, the less via the intermediate ( $\text{HO}_2^-$ ) the oxygen reduction reaction is.

5 That means the higher activity is expected.

[0029]

"the number of the reaction electrons" =  $(I(2 \text{ electrons}) + I(4 \text{ electrons})) / (I(2 \text{ electrons})/2 + I(4 \text{ electrons})/4)$ ,

10 where  $I(2 \text{ electrons}) = -$  "detecting electrode current"/"the rate of capture", and  $I(4 \text{ electrons}) =$  "detecting electrode current" -  $I(2 \text{ electrons})$ .

Wherein, the rate of capture is a value representing how many reaction intermediates occurring at the working  
15 electrode are captured. As the result of the number of the reaction electrons calculated from the ratio of the currents of the working electrode to the detecting electrode, the number of the reaction electrons were 3.90.

20 [0030]

[Example 2]

The electrode catalyst powder was prepared and evaluated as described in Example 1, except for the use of 0.452 g of gadolinium nitrate ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , from Wako  
25 Pure Chemical Industries Ltd.) instead of cerium nitrate. The powder X-ray diffraction of the electrode catalyst powder prepared enabled the detection of Ag and  $\text{Gd}_2\text{O}_3$ . The measurement result of the potential-current



curve by CFDE evaluation is shown in Fig. 2. Further, the number of the reaction electrons were 3.87. The start-up of the oxygen reduction current of Example 2 was higher than that of Example 1 and the oxygen  
5 reduction activity of Example 2 was better than that of Example 1.

[0031]

[Example 3]

The electrode catalyst powder was prepared and  
10 evaluated as described in Example 1, except for the use of 0.440 g of holmium nitrate ( $\text{Ho}(\text{NO}_3)_3$  from Wako Pure Chemical Industries Ltd.) instead of cerium nitrate. The powder X-ray diffraction of the electrode catalyst powder prepared enabled the detection of Ag and  $\text{Ho}_2\text{O}_3$ .  
15 The measurement result of the potential-current curve by CFDE evaluation is shown in Fig. 2. Further, the number of the reaction electrons were 3.91. The start-up of the oxygen reduction current of Example 3 was higher than that of Example 2 and the oxygen reduction activity  
20 of Example 3 was better than that of Example 2.

[0032]

[Comparative Example 1]

The carbon containing 50% by weight of silver was prepared and evaluated as described in Example 1.

25 The powder X-ray diffraction of the electrode catalyst powder prepared enabled the detection of Ag. Further, the observation of the micro-structure was performed with the high resolution analysis transmission

electron microscope. As the result, the particulate silver with 10 to 50 nm was found.

The measurement result of the potential-current curve by CFDE evaluation is shown in Fig. 1.

- 5 The start-up of the oxygen reduction current of Comparative Example 1 was lower than that of Examples 1 to 3 and the number of the reaction electrons of Comparative Example 1 was 3.69 which was lower than that of Examples 1 to 3.

10 [0033]

[Example 4]

(Preparation of a powder for reaction layer)

- As described in Example 1, an electrode catalyst was prepared, which has a particulate silver and a particulate cerium oxide, supported on a carbon carrier. 0.18 g of the carbon particles supporting the resultant electrode catalyst was added to 15 ml of ethanol : water = 1 : 60 (weight ratio), and then 0.04 g of polytetrafluoroethylene dispersion (from Daikin Industries Ltd., POLYFLON<sup>TM</sup> TFE D-1 (solid content: 60% by weight)), followed by stirring for one hour, filtration, and drying at 100°C for 24 hours. Subsequently, dispersion was carried out for 10 minutes, using a sonicator (from Nihon Seiki Seisakusho Co., Ltd.: US-600T), and 30 ml of ethanol was then added, followed by stirring for 30 minutes. After filtration, this was dried at 100°C for 24 hours, followed by pulverization using a mill to provide a powder for the

reaction layer.

[0034]

(Preparation of a powder for gas diffusion layer)

A polytetrafluoroethylene dispersion (from  
5 Daikin Industries Ltd., POLYFLON™ TFE D-1 (solid  
content: 60% by weight)) was added to a mixture of  
carbon black (from Denki Kagaku Kogyo K. K.: Denka Black  
AB-7™) : surfactant (from Rohm and Haas Co.: Triton X-  
100) : water = 1 : 1 : 20 (weight ratio) so as to  
10 provide a carbon black to polytetrafluoroethylene weight  
ratio of 7 : 3, followed by dispersing for 10 minutes  
using a sonicator. Ethanol was then added to aggregate  
particles in the dispersion. Subsequently, suction  
filtration was performed, and the resultant solid  
15 content was dried at 100°C for 24 hours, followed by  
grinding using a mill for pulverization. This powder  
was then stirred in ethanol for one hour to wash and  
remove the surfactant. Thereafter, this was pulverized  
using a mill to provide a powder for gas diffusion  
20 layer.

[0035]

(Preparation of a gas diffusion electrode)

An aluminum foil clarified with acetone was  
placed on the bottom of a die for hot pressing having an  
25 internal diameter of 20 mm, a 100-mesh nickel gauze  
having a wire diameter of 0.1 mm was placed on the  
aluminum foil, and 0.1 g of the powder for gas diffusion  
layer was packed before packing 0.05 g of the powder for

reaction layer, followed by cold pressing.

Subsequently, the die was held in a hot pressing machine (from Tester Sangyo Co., Ltd.: SA-303) while maintaining at 370°C to perform hot pressing at 60 kg/cm<sup>2</sup> for one minute to provide a gas diffusion electrode.

[0036]

(Evaluation of electrochemical characteristics of the gas diffusion electrode)

10           The gas diffusion electrode obtained was mounted in a cell for evaluation of electrochemical characteristics, and evaluated for electrochemical characteristics of oxygen reduction reaction by supplying pure oxygen at 50 ml/min from the gas diffusion layer side in a 33 wt% sodium hydroxide aqueous solution at 80°C.

20           The cell for electrochemical evaluation has a structure in which passages for oxygen supply and for discharge are formed and the gas diffusion electrode is mounted through an O-ring to keep airtightness in the cell. After placing the cell in an electrolytic bath, the evaluation of electrochemical characteristics was performed by supplying oxygen from the gas diffusion layer side at a state where only the reaction layer side was exposed to the 33 wt% sodium hydroxide aqueous solution at 80°C. The effective surface area of the gas diffusion electrode is 3.14 cm<sup>2</sup>. HC-113 from Hokuto Denko Co., Ltd. was used as a current pulse generator,

and a platinum gauze and a mercury/mercury oxide electrode were employed as a counter electrode and a reference electrode, respectively.

[0037]

5                   The result of the electrochemical evaluation is depicted in Fig. 3. The horizontal and vertical axes represent current density and potential with respect to the mercury/mercury oxide electrode, respectively. As shown in Fig. 3, excellent oxygen reduction activity was  
10 observed compared to those of the electrode catalyst supporting only the particulate silver on the carrier of the particulate carbon.

[0038]

[Comparative Example 2]

15                   The carbon containing 50% by weight of silver was prepared as described in Example 1. A gas diffusion electrode was prepared and evaluated as described in Example 4, except for the use of the electrode catalyst. The result of evaluation obtained is shown in Fig. 3.

20 [0039]

[Advantages of the Invention]

                  The electrode catalyst of the present invention exhibits higher oxygen reduction activity as an electrode catalyst for oxygen reduction than a  
25 conventional carbon electrode catalyst supporting only the particulate silver. Use of the electrode catalyst of the invention for a gas diffusion electrode may reduce oxygen reduction overvoltage in the electrolysis

of an alkali metal halide aqueous solution such as brine using an ion exchange membrane. As a result, it has become possible to reduce the electric power used for electrolysis to manufacture products such as chlorine and caustic soda, thus resulting in a lower cost.

[Brief Description of the Drawings]

[Fig. 1]

An illustrative picture of an evaluation device using CFDE.

10 [Fig. 2]

An illustration of the result of evaluating electrode catalysts in Examples and Comparative Example, using CFDE.

[Fig. 3]

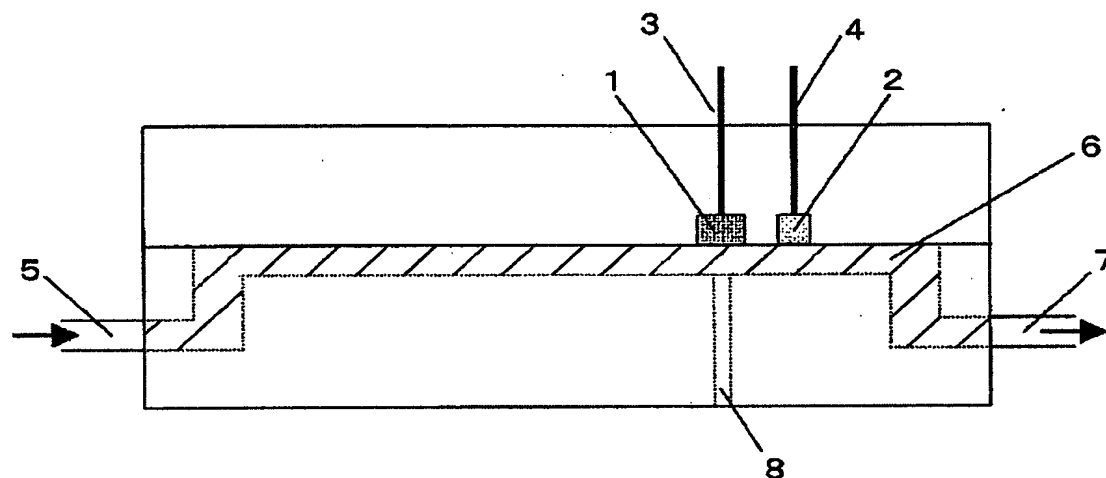
15 An illustration of electrochemical characteristics of gas diffusion electrodes in Examples and Comparative Example.

[Description of Reference Numerals]

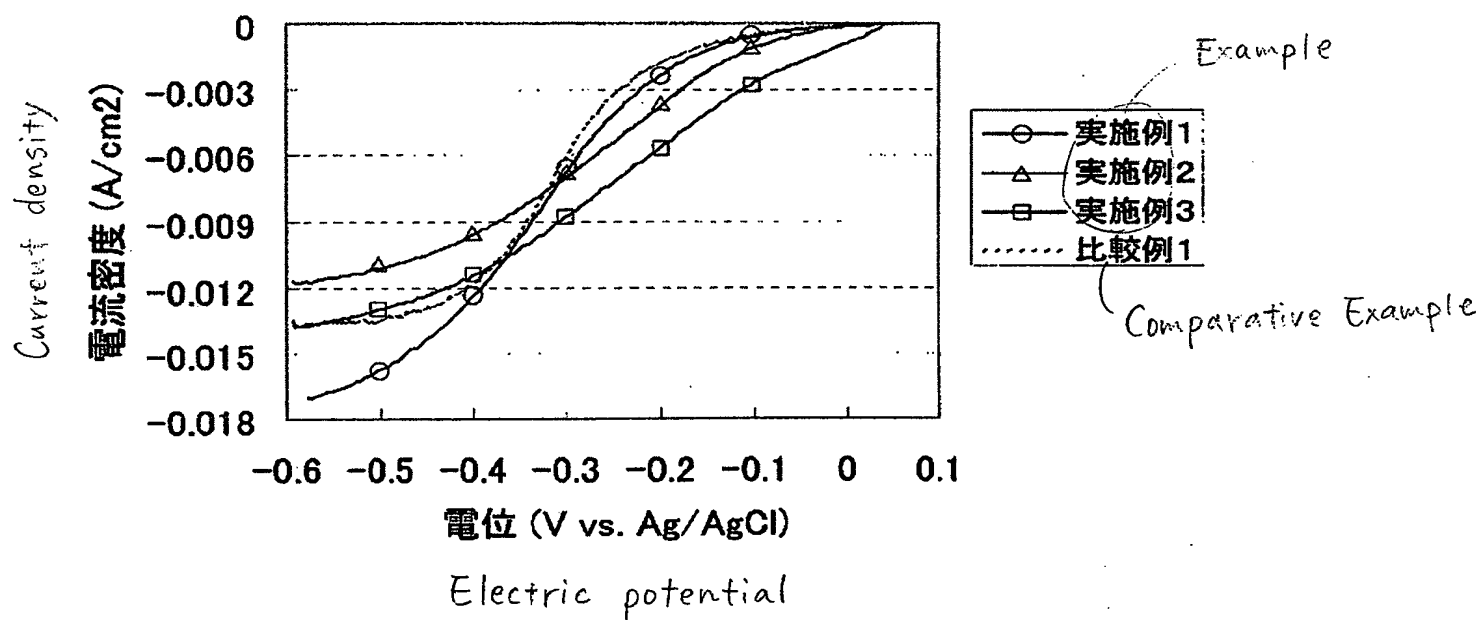
- |   |                            |
|---|----------------------------|
| 1 | working electrode          |
| 2 | detecting electrode        |
| 3 | working electrode wiring   |
| 4 | detecting electrode wiring |
| 5 | electrolyte passage        |
| 6 | electrolyte inlet          |
| 7 | electrolyte outlet         |
| 8 | conductive passage         |

【書類名】 図面

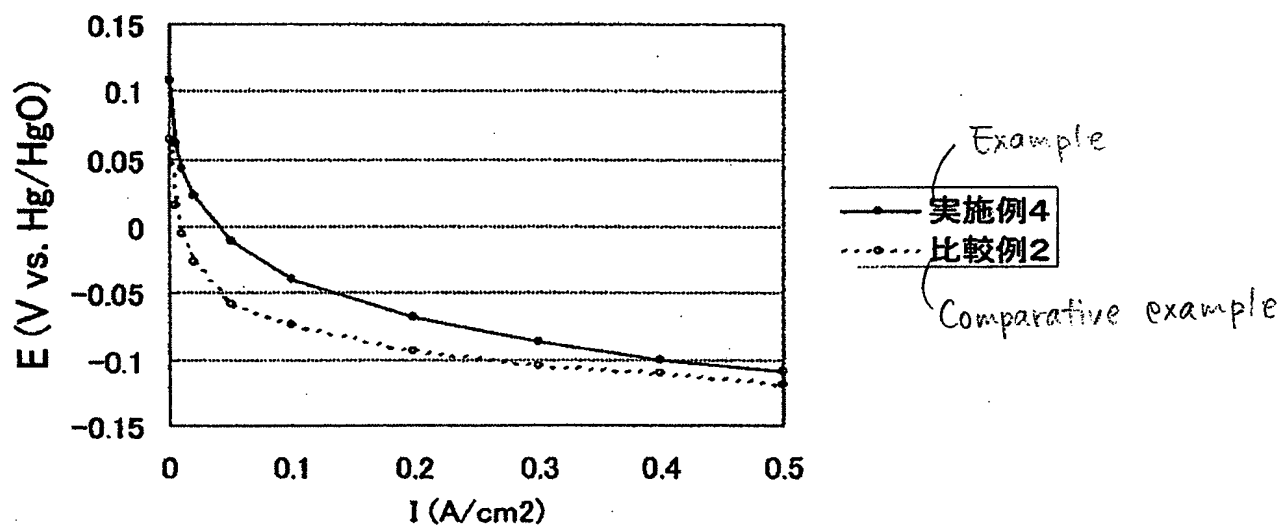
【図1】



【図2】



【図3】





[Kind of Document]    Abstract

[Abstract]

[Problem]

To provide a preferred electrode catalyst for oxygen reduction. To provide the electrode catalyst exhibiting higher oxygen reduction activity than a conventional carbon electrode catalyst supporting a particulate silver.

[Solution]

An electrode catalyst characterized by including a catalyst supported on a conductive carrier wherein the catalyst is a mixture of a particulate silver and at least one particulate rare-earth oxide.

[Selected Drawing]    None